



# Conductivity study on ionic liquid/polymer complexes

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## Abstract

Ternary salt mixtures, consisting of triethylmethylammonium benzoate (TEMAB), lithium acetate (LiOAc) and lithium bis(trifluoromethylsulfonyl) imide (LiTFSI), form stable molten salts at moderate temperatures at certain compositions. A typical composition of the molten salts is TEMAB/LiOAc/LiTFSI = 7/2/1 in molar ratio, and the glass transition temperature, the crystallization temperature and the melting temperature are  $-52^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$  and  $55^{\circ}\text{C}$ , respectively. Quenched salt mixture having the above composition forms a stable supercooled liquid at room temperature, and the ionic conductivity is  $10^{-4} \text{ Scm}^{-1}$  at  $30^{\circ}\text{C}$  and  $10^{-3} \text{ Scm}^{-1}$  at  $60^{\circ}\text{C}$ . Some commercially available polymers such as polyacrylonitrile and poly(vinyl butyral) are compatible with the salt mixture to result in film forming polymer electrolytes with 1-2 order(s) of magnitude of loss of the molten salt conductivity.

**Keywords:** Polymer electrolyte; Molten salt; Ionic liquid; Ionic conductivity

## 1. Introduction

A rather new concept of addition of small amounts of polymers to real or supercooled ionic liquids has been reported [1-7] to combine high ionic conductivity and rubbery compliance in resulting polymer electrolytes. The high conductivity and rubbery compliance are due to the ionic liquids and to entanglement effects of the polymers, respectively. The concept may come from the limitation in conductivity of conventional polyether-based polymer electrolytes, where, in contrast, small amounts of salts are dissolved in the polymers, and the ionic motion is coupled with the segmental motion. The limitation is based on the inconsistency of simultaneous increases in both the number of carrier ions and their mobility, because the increase in salt concentration causes the increase in glass transition

temperature ( $T_g$ ) of the host polymers. We have explored [1-3] that the addition of small amounts of high molecular weight poly(1-butyl-4-vinylpyridinium halide) to room temperature molten salts, consisting of 1-butylpyridinium halide and aluminium chloride, yields new polymer electrolytes having higher ionic conductivity than  $10^{-3} \text{ Scm}^{-1}$  at room temperature and rubbery compliance.

The present work is to extend the new concept to lithium-ion-conducting polymer electrolytes. Angell et al. have recently reported [4-7] that so-called "polymer-in-salt" electrolytes, consisting of a supercooled mixture of lithium salts and a small quantity of a polymer like high molecule weight poly(ethylene oxide), give ideal polymer electrolytes for lithium battery application, because of the combination of  $\text{Li}^+$  ion conduction and rubbery compliance. Although  $T_g$ 's of the supercooled mixtures of lithium salts lie below ambient temperatures, the mixtures are thermodynamically unstable at room temperature,

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because of melting temperatures ( $T_m$ ) of the mixtures being higher than room temperature [4-7]. Thus, crystallization of supercooled mixtures might be, in general, a serious drawback of  $\text{Li}^+$  conducting polymer-in-salt electrolytes in terms of the stability of the conductivity [8]. The present study is an attempt to prepare  $\text{Li}^+$ -conducting real ionic liquids in the mixtures, consisting of triethylmethylammonium benzoate (TEMAB), lithium acetate (LiOAc) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI). Preliminary results on compatibility of the ionic liquids with some polymers and on ionic conductivity of the resulting polymer electrolytes are also presented.

## 2. Experimental

LiOAc (Junsei Chemical, mp: 280°C) and LiTFSI (kindly supplied by M. Gauthier of IREC, mp: 237°C) were dried under high vacuum at 180°C for 30 h before use. TEMAB (Mitsubishi Chemical) was recrystallized three times from acetone and dried under vacuum at 70°C, mp: 99°C. Polyacrylonitrile (PAN, Aldrich) and poly(vinyl butyral) (PVBu, Sekisui Chemical), which is acetalized poly(vinyl alcohol) by *n*-butylaldehyde, were dried under vacuum.

In an argon filled glove box, weighed amounts of LiOAc, LiTFSI and TEMAB were mixed in glass vials, heated to a temperature just below decomposition temperature of TEMAB, ca. 200°C, and quenched to room temperature. In the case of LiOAc/LiTFSI binary mixtures, the mixtures were heated up to a temperature, where homogeneous melts were obtained, and quenched to room temperature. To a certain composition of the ternary mixtures (TEMAB/LiOAc/LiTFSI = 7/2/1 in molar), which formed a room temperature ionic melt, PAN and PVBu were complexed in order to obtain film forming polymer electrolytes. PAN and PVBu were dissolved in *N,N*-dimethylformamide, and to each solution were added the molten salt to yield a homogeneous viscous solution, which was cast on a glass plate, followed by the complete evaporation of the solvent.

Ionic conductivity of both of the molten salts and the polymer electrolytes was determined by complex

impedance measurements using a computer controlled HP-4192A LF impedance analyzer.

For differential scanning calorimetry (DSC) measurements of the salt mixtures, the quenched samples were sealed in Al pans in an argon filled glove box, and DSC thermograms were measured by using a Seiko Instruments DSC 220C at a heating rate of 10°C/min under nitrogen atmosphere.

## 3. Result and discussion

In order to realize real ionic liquids at ambient temperatures (room temperature molten salts), the phase diagram for the mixtures of LiOAc and LiTFSI was first explored. Fig. 1 shows the phase diagram for the LiOAc and LiTFSI mixtures. LiOAc is a glass forming salt, and LiTFSI is a newly developed and high dissociative salt [9]. With the addition of LiTFSI to LiOAc,  $T_m$  and  $T_g$  of the mixtures continuously decrease up to ca. 50 mol% of LiTFSI. This behaviour is similar to that observed in the lithium salt mixtures where a certain lithium salt other than LiTFSI is added to LiOAc [4]. At 50 mol% of LiTFSI,  $T_m$  and crystallization temperature ( $T_c$ ) are close to 150°C, whereas  $T_g$  is 33°C. Thus, the quenched mixture behaves as a supercooled liquid at around room temperature. However, vis-

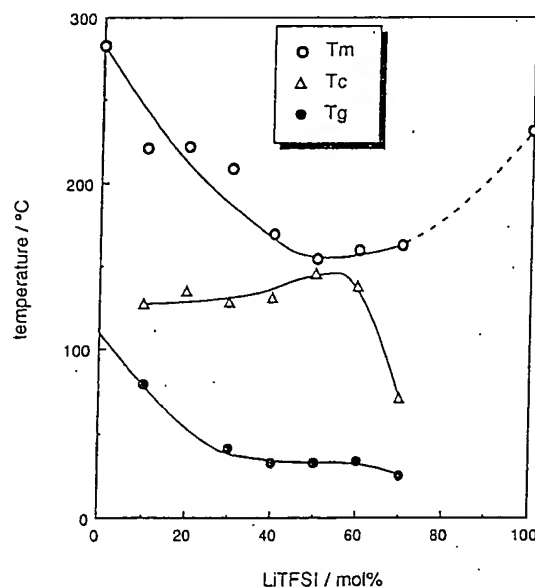


Fig. 1. Phase diagram for LiOAc and LiTFSI binary mixtures.

cosity of the mixture is quite high, and the ionic conductivity is only  $10^{-6} \text{ Scm}^{-1}$  even at  $100^\circ\text{C}$ . This combination was not suitable to be complexed with polymers to form polymer electrolytes.

The second strategy which we adopted to obtain stable ionic liquids is to add TEMAB to the LiOAc/LiTFSI mixtures. TEMAB has a relatively low  $T_m$  ( $99^\circ\text{C}$ ) in organic ammonium salts and aliphatic ammonium salts like TEMAB is electrochemically stable up to reduction potential of  $\text{Li}^+$  ion. Thus, TEMAB was used to reduce  $T_m$  of the LiOAc/LiTFSI mixtures, serving as a stable ionic solvent for the mixtures. Fig. 2 shows the states of the ternary salt mixtures plotted against the compositions. Typical DSC thermograms of the salt mixtures are shown in Fig. 3, where the numerals in the thermograms correspond to the composition plots having the same numerals in Fig. 2. In Fig. 2, solid circles represent the ternary salt compositions that are inhomogeneous even at  $200^\circ\text{C}$ , whereas open symbols (circles, hexagons and squares) represent the compositions that form homogeneous mixtures at  $200^\circ\text{C}$ . The compositions represented by the open symbols can be divided into three groups, depending on the states

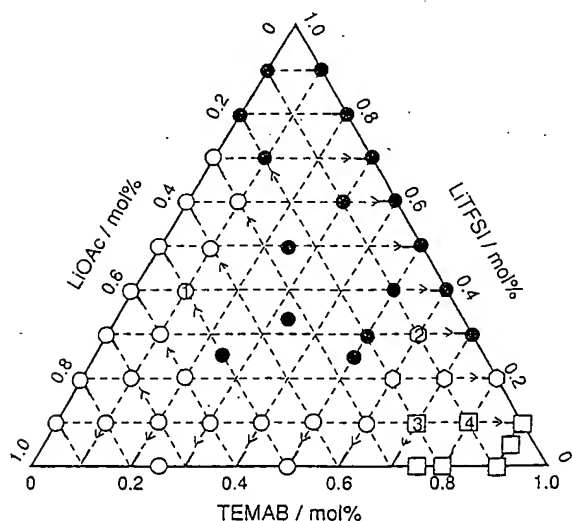


Fig. 2. States of ternary mixtures, consisting of TEMAB, LiOAc and LiTFSI, plotted against compositions: ●, inhomogeneous at  $200^\circ\text{C}$ ; ○, homogeneous at  $200^\circ\text{C}$  and glassy or highly viscous at room temperature (rt) by quenching from  $200^\circ\text{C}$ ; ⬡, homogeneous at  $200^\circ\text{C}$  and inhomogeneous at rt by quenching; □, homogeneous at  $200^\circ\text{C}$  and ionic liquids at rt by quenching. The compositions where numerals are cited in the symbols correspond to the thermograms of Fig. 3 having the same numerals.

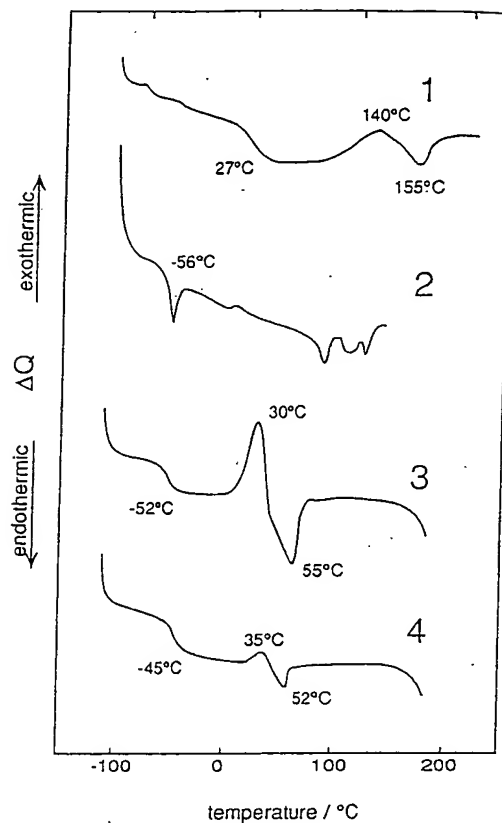


Fig. 3. DSC thermograms of typical ternary mixtures. TEMAB/LiOAc/LiTFSI: 1, 0.1/0.5/0.4; 2, 0.6/0.1/0.3; 3, 0.7/0.2/0.1; 4, 0.8/0.1/0.1.

at room temperature after quenching from  $200^\circ\text{C}$ . Open circles correspond to the compositions that form either glasses or highly viscous supercooled liquids at room temperature. Open hexagons correspond to the compositions that result in inhomogeneous mixtures after quenching. Ternary salt mixtures having the compositions indicated by open squares form ionic melts at room temperature by quenching. These differences are clearly reflected in the DSC thermograms shown in Fig. 3. The diagram shown in Fig. 2 reveals the following facts. The binary compatibilities between TEMAB and LiOAc and LiTFSI are rather good, whereas the compatibility between TEMAB and LiTFSI is poor, especially when LiTFSI composition is high. Reflecting these binary compatibilities in the ternary mixtures, homogeneous melts at  $200^\circ\text{C}$  (open symbols in Fig. 2) are obtained when the composition of LiTFSI is low or when the composition of TEMAB is low. For the salt mixtures having low TEMAB and high

LiOAc compositions, the quenched salts are glasses or highly viscous supercooled liquids, as seen in a typically shown DSC thermogram 1 in Fig. 3. The states of the mixtures are very close to those of the binary mixtures of LiOAc and LiTFSI, as mentioned in Fig. 1. In contrast, for the salt mixtures having high TEMAB and low LiTFSI compositions, the quenched salts form ionic melts. Typical compositions of the ionic melts are TEMAB/LiOAc/LiTFSI-7/2/1 and 8/1/1. DSC results for these two compositions are shown in the thermograms 3 and 4 of Fig. 3.  $T_m$  of the mixtures are 55°C and 52°C, respectively, and  $T_g$ 's are well below room temperature. The quenched salts are found to form stable supercooled liquids at room temperature for at least a few days.

In Fig. 4 is shown temperature dependence of ionic conductivity for the salt mixture of TEMAB/LiOAc/LiTFSI = 7/2/1, abbreviated as (721) in the figure. The temperature dependence was measured with descending temperature. The salt mixture was kept at each temperature for ca. 1 h for reaching thermal equilibrium. The ionic conductivity is  $10^{-4}$  Scm $^{-1}$  at 30°C and  $10^{-3}$  Scm $^{-1}$  at 60°C. The continuously changing conductivity indicates that crystallization of the melt does not occur down to

-10°C, within the time scale of measurements. The salt mixture having the composition of TEMAB/LiOAc/LiTFSI = 8/1/1 gave almost the identical conductivity with the present mixture.

Compatibility of the ionic melts with polymers has been explored by using several commercially available polymers. Up to now, PAN and PVBu give reasonable compatibility with the ionic melts. Ionic conductivity of the polymer electrolytes is shown in Fig. 4. The addition of the polymers to the ionic melts imparts film forming property to the resulting polymer electrolyte films, with a loss of 1-2 order(s) of magnitude of the molten salt conductivity. However, with standing the polymer electrolytes at room temperature for a long time, crystallization and phase separation of the salt mixtures were observed. To explore other properties than ionic conductivity, such as transport number and electrochemically stable potential-window, is currently being conducted in our group.

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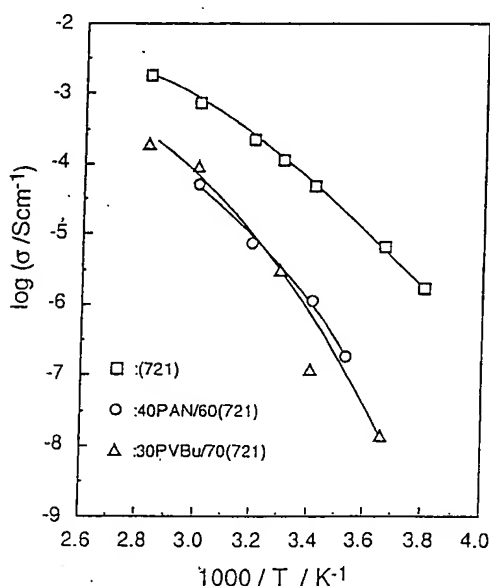


Fig. 4. Temperature dependence of ionic conductivity for ionic melt (721) (TEMAB/LiOAc/LiTFSI = 7/2/1) and its polymer complexes with polyacrylonitrile (PAN) and poly(vinyl butyral) (PVBu). The composition of the polymers are represented in unit mol % in the figure.